The Potentiometric Determination of Gold in Gold Plating Solution with Silver Ions

Walter S. Selig

This paper was prepared for submittal
to
Plating and Surface Finishing

October 1984

Lawrence
Livermore
National
Laboratory

DISCLAIMER

The Potentiometric Determination of Gold in Gold
Plating Solutions by Titration with Silver Ions

by Walter S. Selig

ABSTRACT

Gold in gold cyanide plating solutions and in solid potassium aurocyanide can be determined by titration with a standard solution of silver nitrate. The monovalent gold need not be converted to the trivalent state with aqua regia prior to its determination. Free cyanide and aurocyanide can be sequentially determined in the same solution with one titrant. Alternatively, cyanide may be complexed by formaldehyde. Chloride also does not interfere in the determination of gold cyanide and may also be determined with the same titrant.

1. INTRODUCTION

The assay of gold in so-called "gold cyanide" -- actually aurocyanide, $Au(CN)_2$ -- is usually required on the plating baths. It may also be required on the aurocyanide salt prior to the preparation of the plating baths.

Titrimetry, in general, is considerably faster than gravimetry, and more precise and less costly than atomic absorption spectrometry, methods which are used in the determination of gold. According to Kolthoff and Elving[1] all titrimetric methods for the determination of gold are based upon the reduction of gold(III),

either to the metal or to monovalent gold. Indeed, the methods

given for aurocyanide in gold plating solutions in the

Electroplaters Process Control Handbook[2] are based either on the

reduction of gold(III) with iodide according to the reaction

$$Au^{3+} + 2I^- \longrightarrow Au^+ + I_2 \qquad (1)$$

or on a similar reduction with sulfur dioxide

$$2Au^{3+} + 3SO_2 + 3H_2O \longrightarrow 2Au + 3SO_3 + 6H^+ \qquad (2)$$
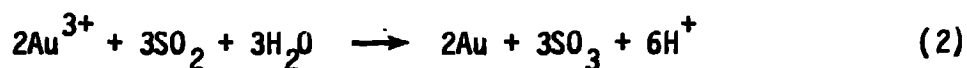
Both methods require conversion of the monovalent gold in

aurocyanide to trivalent gold by means of aqua regia, which is a

time-consuming process requiring handling of corrosive acids and

operations in a hood.

In this paper we propose a new titrimetric method for the

direct determination of aurocyanide by potentiometric titration with

a standard silver nitrate solution according to the reaction

$$Ag^+ + Au(CN)_2^- \longrightarrow Ag[Au(CN)_2] \downarrow \qquad (3)$$
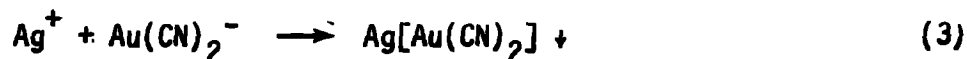
Our method does not require conversion of the monovalent gold to the

trivalent state with aqua regia. Other advantages are (1) the

presence of excess cyanide can be detected immediately from the

initial emf of the solution to be titrated; (2) cyanide and

aurocyanide can be determined by sequential titration with one titrant. Alternatively, the cyanide can be complexed with formaldehyde and the aurocyanide determined alone; (3) chloride does not interfere and can, in fact, also be determined by sequential titration with silver nitrate.

2. Comments on Potentiometric Titrations

A good introduction to titrimetric analysis is given by Watters in Kolthoff and Elving's Treatise on Analytical Chemistry.[3] The theory and techniques of potentiometric titrations are also discussed in texts on electroanalytical chemistry.[4,5] It should be recalled that the use of a titration technique requires a means of detecting the endpoint precisely, and that this endpoint should correspond closely to the equivalence point of the stoichiometric reaction. In a potentiometric titration the endpoint is signalled by a change in the electromotive force (emf) between two electrodes, the sensor and the reference, immersed in the solution being titrated. The reaction of importance to us (equation 3) is a precipitation titration and can be monitored by an electrode which responds to the activity of the precipitating cation, the silver ion. This electrode can be a silver wire, or one of the more recently developed silver ion-selective electrodes.

The endpoint of a potentiometric titration usually occurs at the point of maximum potential change, which is where $\Delta E/\Delta V$ is at maximum (E is the emf, and V is the volume of titrant added), or where the second derivative, $\Delta^2 E/\Delta V^2$, is zero.

In the evaluation of the titration method described here, an automatic titrator was used. Modern automatic titrators have the capability of locating and calculating the endpoints of titrations, using one of the above-mentioned methods. However, any type of titration equipment, such as a buret in combination with a pH/millivolt meter, is suitable. In this case, the titration and the evaluation of the titration curve obviously will be more laborious. If the titration is performed manually it is recommended that as the titration endpoint is approached (as evidenced by the increasing potential jumps), the titrant be added in equal increments (0.05 ml) and the emf at each point recorded. This is continued until the titration has proceeded past the endpoint, as indicated by the deceasing potential jumps. The maximum slope of $\Delta E/\Delta V$ is then calculated as described in the text by Lingane.[5]

3. **EXPERIMENTAL**

    3.2. **Equipment Used**

    The titrant was an aqueous 0.01 M silver nitrate solution prepared from reagent grade material by dissolving 1.70 g of the salt in distilled water and diluting to 1 liter. It should be stored in an amber bottle because the solution is light-sensitive. The procedure for standardization is given in Section 3.2.

    The titration system was controlled by a Tektronix 4051 graphics system previously described.[6] However, as already mentioned, any type of titration equipment, such as a buret in combination with a pH/millivolt meter, is suitable. The sensing

electrode was an Orion 94-16A silver/sulfide ion-selective electrode. The reference electrode was a double-junction Orion 90-02 with a salt-bridge of 0.1 N sodium nitrate.

Titrations were carried out in 50-mL beakers, containing aliquots of the standards or solutions to be analyzed, diluted to approximately 25 mL. Titration rates were kept constant at 0.3 mL/min. Stirring was provided by a magnetic stirrer. The stirring motor was separated from the titration vessel by a water cooling plate and a grounded aluminum plate. Titrations were performed at 23 ± 1°C.

3.2. Standardization of Silver Nitrate Titrant

1. Prepare a stock solution of potassium bromide from reagent grade material to contain approximately 6 mg of potassium bromide per 10 ml.

2. Deliver 10.00-mL aliquots of this solution into a 50-mL beaker containing a stirring bar and dilute to 25 mL with distilled water.

3. Titrate potentiometrically using the automatic titrator (or other available equipment).

4. Calculate the mean normality from at least three runs according to the formula:

Normality of silver nitrate = (mmol of bromide taken)/(ml of titration)

5. For the highest accuracy it is desirable to standardize the titrant every two or three days.

3.3 **Assay of Gold in Potassium Aurocyanide, KAu(CN)$_2$**

1. Weigh 130 to 150 mg of gold cyanide accurately to
±0.1 mg into a 100-mL volumetric flask, dissolve in
distilled water, and dilute to volume.

2. Use a 5 to 15 mL aliquot to yield a titration volume
between 2 and 8 mL (4 to 15 mg of gold).

3. Deliver this amount accurately (by pipet) into a 50-mL
beaker containing a stirring bar, and dilute to 25 mL
with distilled water.

4. For automatic titrators enter the titer calculated as
follows:

Titer = (normality of silver nitrate)(196.967)

The results will be in mg gold.

5. Titrate potentiometrically with silver nitrate and
calculate the endpoint either automatically on
computer-controlled titrator, or as outlined in the
section in Reference 5 on potentiometric titrations.

6. From the amount of sample per aliquot, the percentage
of gold in the original sample can be calculated.
(The pure material contains approximately 68% of gold.)

3.4. **Evidence of Free Cyanide**

The initial emf of cyanide-free potassium aurocyanide
is near -50 mV with the electrode pair used. Free
cyanide will lower this voltage, the amount depending on
the amount of cyanide present. A mere one mg of free
cyanide will lower the initial emf by as much as 500 mV.

3.5 <u>Determination of Gold Cyanide Alone in the Presence of</u>

<u>Excess Cyanide</u>

If the initial emf prior to a titration of gold

cyanide shows the presence of free cyanide by a markedly

lowered initial emf, proceed as follows:

1. While monitoring the pH with a pH meter, add

   formaldehyde (A.C.S. reagent, 36-38% assay by weight)

   solution until the pH is 5-6.

2. Let the solution stand for approximately 15 min.

3. Proceed with the titration of gold cyanide as in

   section 3.3.

3.6. <u>Estimation of Free Cyanide and Gold Cyanide</u>

If free cyanide as well as gold cyanide are present, titration

with silver nitrate will result in two breaks in the titration

curve. Proceed as outlined in Section 3.3 using merely the

normality of the silver nitrate titrant as the computer input in

step (4).

The first endpoint break will be due to the complexation of

cyanide (see Section 4) and we shall designate the volume as "a".

The second titration endpoint will be due to the precipitation of

aurocyanide as shown in reaction (3) and to the precipitation of

silver cyanide, as shown in Section 4 (equation 5). We shall

designate this volume as "b". The titration volumes are calculated

as follows:

Volume of titrant for free cyanide = a

Volume of titrant for aurocyanide = b - 2a

The volumes multiplied by the titrant normality yield the mmol of cyanide or aurocyanide, respectively. To convert mmol into mg, multiply by 52.04 for cyanide, and by 196.967 for gold.

It should be pointed out that if large amounts of free cyanide are present the difference between the second and first endpoint breaks may be too large to be practical for the 10-ml buret ordinarily used with our titrator. In this case, complexation of the cyanide with formaldehyde solution is recommended prior to the determination of aurocyanide. If an estimate of the free cyanide is desired, a smaller aliquot of solution should be used for titration, and only the first endpoint needs to be evaluated.

3.7. Determination of Aurocyanide and Chloride

If chloride is present in the solution two endpoint breaks will result if the titration with silver nitrate is carried to completion. The first endpoint break will be due to aurocyanide, while the second break will be due to chloride plus aurocyanide. The titration volume for chloride equals the difference between the second and first endpoint break. The conversion factor for chloride is 35.45. Refer to p. 11 for the case when, in addition, cyanide is present.

4. RESULTS AND DISCUSSION

Titrimetric methods for the determination of gold in gold cyanide and gold cyanide plating solutions have heretofore required oxidation of gold from the monovalent to the trivalent state. After this initial conversion, various methods of determination are

available, such as the redox reactions shown in equations (1) and (2) in Section 1. Another technique, controlled potential coulometry, has been used at our Laboratory for many years as the primary assay technique for plating solutions as described in this Journal[7] and elsewhere.[8] This technique also requires that gold be converted to the trivalent state. The sparingly soluble silver salt of the aurocyanide cation, prepared according to equation (3) has been known since 1925.[9] However, the reaction forming this salt has, to our knowledge, not been used previously for the determination of aurocyanide. A typical curve for the titration of 0.025 mmol of aurocyanide with 0.01 M silver nitrate is shown in Fig. 1. An aqueous solution of potassium aurocyanide has a pH of approximately 6.6. The titration is also feasible in nitric acid solutions down to a pH of 1.25. The aurocyanide complex is quite stable in acid solution; the log of the stability constant is 38.3.[10]

Some of the precipitates were recovered by filtration, washing with distilled water and air-drying to constant weight. Elemental analysis of the recovered material confirmed the stoichiometry of the reaction: for $Ag[Au(CN)_2]$ calculated percent. C 6.73, N 7.85; found percent, C 7.03, N 7.71.

Cyanide can also be determined by titration with silver nitrate.[11] The reactions are as follows:

$$Ag^+ + 2CN^- \longrightarrow Ag(CN)_2^- \tag{4}$$

and

$$Ag^+ + Ag(CN)_2^- \longrightarrow Ag[Ag(CN)_2]\downarrow = 2AgCN \downarrow \tag{5}$$
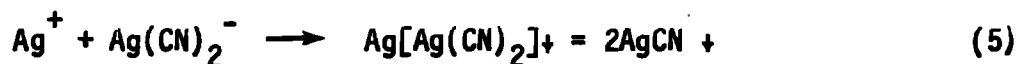
Reaction (4) yields a soluble complex and a steep titration break while reaction (5) yields a fairly shallow endpoint break and a precipitate. A typical titration curve is shown in the original publication.[11] When both free cyanide and aurocyanide are present in solution, the first endpoint break upon titration with silver nitrate is due to reaction (4), while the second endpoint break is due to the sum of reactions (3) plus (5). A typical titration curve for cyanide and aurocyanide is shown in Fig. 2.

Free cyanide can be masked or complexed by formaldehyde solution according to

$$HCN + HCHO \longrightarrow CN.CH_2OH \tag{6}$$

forming cyanohydrin. This reaction proceeds to completion at room temperature within 15 min.

When both free cyanide and aurocyanide are present, the results for the aurocyanide determination are less accurate than when aurocyanide alone is present, probably because of coprecipitation of $[Ag(Au(CN)_2]$ and $AgCN$. The results of the assay of solid potassium aurocyanide as well as for some gold cyanide plating baths are shown in Table I. The previously used controlled-potential coulometric method[7,8] was compared with the new method. In general, the standard deviations for the new method were lower than those for controlled potential coulometry, which is not surprising because the latter method requires an acid boil-down and treatment with aqua regia prior to measurement of the gold. This is probably the step that introduces the most errors because of the possible loss of gold. The coulometric measurement step itself is much more precise.[8] Three samples of the salt were also assayed by a gravimetric method in which the gold was precipitated and weighed as the metal. Not surprisingly, the results were about midway between those obtained by controlled-potential coulometry and direct titration.

Chloride, as well as other halides, are also determined commonly by titration with silver nitrate according to

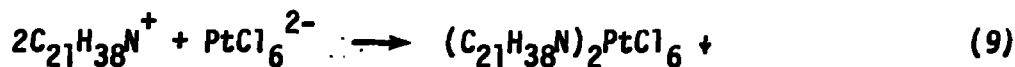$$Ag^+ + X^- \longrightarrow AgX \downarrow \tag{7}$$

Where X may be chloride, bromide, or iodide. Only chloride is of

concern in cyanide plating baths. Aurocyanide and chloride in the same solution yield two endpoint breaks with silver nitrate, the first due to the aurocyanide, and the second due to the sum of aurocyanide plus chloride. A typical titration curve for aurocyanide and chloride is shown in Fig. 3. Finally, aurocyanide, cyanide, and chloride can be estimated in the same solution, yielding three distinct endpoint breaks: The first break is the cyanide break (equation 4), the second is the sum of cyanide plus aurocyanide (equations 3 plus 5), and the third is the total of all the ingredients titratable with silver nitrate. When the three anionic species were present together, the second break was found to be rather poor, not yielding accurate results.

Finally, we would like to make a few comments on the determination of gold and platinum in _acid_ solutions. We have previously found that either of these metals alone, or their sum can be determined as the chloro complex by titration vs cetylpyridinium chloride[12] according to the reactions:

$$C_{21}H_{38}N^{+} + AuCl_{4}^{-} \longrightarrow (C_{21}H_{38}N)AuCl_{4} \downarrow \tag{8}$$

and

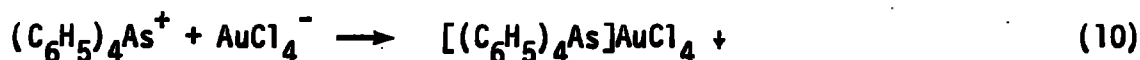$$2C_{21}H_{38}N^{+} + PtCl_{6}^{2-} \longrightarrow (C_{21}H_{38}N)_{2}PtCl_{6} \downarrow \tag{9}$$

where $C_{21}H_{38}N^{+}$ is the cetylpyridinium cation.

If differentiation and quantitation of both precious metals is required, one can make use of the fact that another titrant, tetraphenylarsonium chloride, will react stoichiometrically at pH 0.5 to 1 with $AuCl_{4}^{-}$ according to the reaction

$$(C_{6}H_{5})_{4}As^{+} + AuCl_{4}^{-} \longrightarrow [(C_{6}H_{5})_{4}As]AuCl_{4} \downarrow \tag{10}$$

but will not react with $PtCl_{6}^{2-}$. Thus, the sum of the two precious metal anions can be determined by titration with cetylpyridinium chloride in one aliquot, while $AuCl_{4}^{-}$ alone can be determined by titration vs tetraphenylarsonium chloride in another aliquot. For details the original work should be consulted.[12]

In conclusion, a new technique for the determination of gold in gold cyanide plating baths by titration vs silver nitrate has been described. Its main merit is the avoidance of the conversion of monovalent gold to the trivalent state by aqua regia. This pretreatment required for other methods of determination is time consuming and is probably the step that introduces most errors because of the possible loss of gold in the course of wet-ashing and acid-fuming of the sample. In addition, free cyanide may be estimated during the same titration and, similarly, chloride can be determined.

ACKNOWLEDGMENT

The writer thanks Rosalind W. Swansiger for carrying out the controlled-potential coulometric determinations, and to Randy E. Benson for the elemental analysis.

REFERENCES

1. M. Kolthoff and P. J. Elving (eds.), Treatise on Analytical Chemistry, Part II, Vol. 4, Wiley, New York, 1966, p. 91.

2. D. G. Foulke (ed.), Electroplaters' Process Control Handbook, Revised ed., Robert E. Krieger, Huntington, NY, 1975, pp. 195-197.

3. J. I., Watters, Titrimetric Analysis: Introduction, in Treatise on Analytical Chemistry (I. M. Kolthoff and P. J. Elving, eds.), Part I, Vol, 11, Wiley-Interscience, New York, 1975, pp. 6845-6962.

4. N. H. Furman, Potentiometry, in Treatise on Analytical Chemistry (I. M. Kolthoff and P. J. Elving, eds.), Part I, Vol. 4, Interscience, New York, 1963, pp. 2269-2300.

5. J. J. Lingane, Electroanalytical Chemistry, Interscience, New York, 2nd ed., 1958, p. 91.

6. W. Selig, Mikrochim. Acta [Wien] 1978 II, 75.

7. J. E. Harrar and M. C. Waggoner, Plating Surf. Fin. 68, 41 (1981).

8. J. E. Harrar and F. B. Stephens, J. Electroanal. Chem. 3, 112 (1962).

9. A. Bodensiek, Diss. Hannover T. H., 1925, 19; through Gmelin Handbuch der Anorganischen Chemie, System Nummer 62: Gold, 8th ed., Verlag Chemie, Weinheim, Germany, 1954, p. 767.

10. L. G. Sillen, Stability Constant, Section I: Inorganic Ligands, Special Publication No. 17, The Chemical Society, London, 1964.

11. F. J. Conrad, Talanta 18, 952 (1971).

12. W. S. Selig, Z. anal. Chem. (in press).

FIGURE CAPTIONS

Fig. 1   Titration curve of approximately 5 mg of gold as $Au(CN)_2^-$
with 0.01 M silver nitrate

Fig. 2   Titration curve of approximately 5 mg of gold as $Au(CN)_2^-$ in
the presence of about 0.3 mg of free cyanide.

Fig. 3   Titration curve of approximately 5 mg of gold as $Au(CN)_2^-$ in
the presence of about 3.5 mg of chloride.

Fig. 4   Titration curve of approximately 5 mg of gold as $Au(CN)_2^-$ in
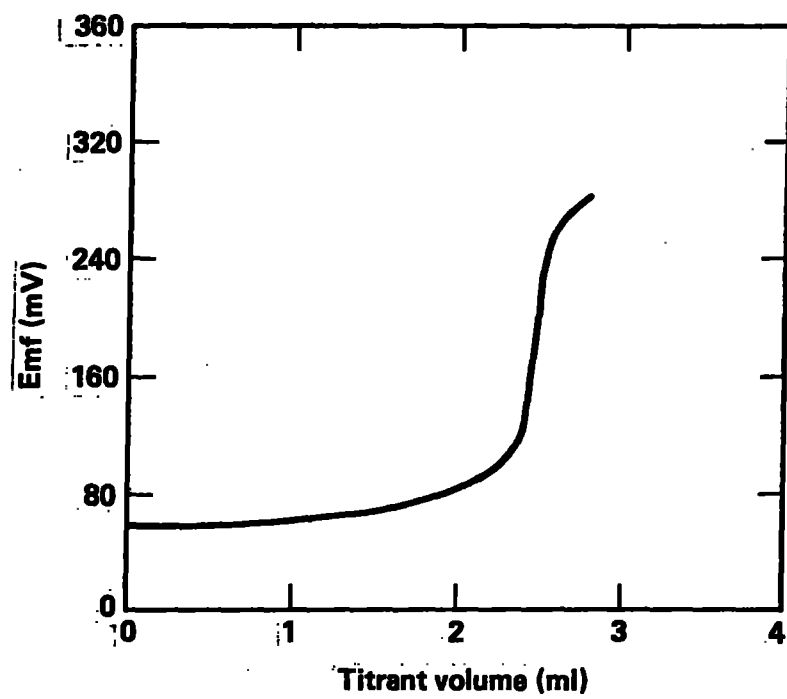the presence of free cyanide and chloride.

Fig. 1

Fig. 2

Fig. 3
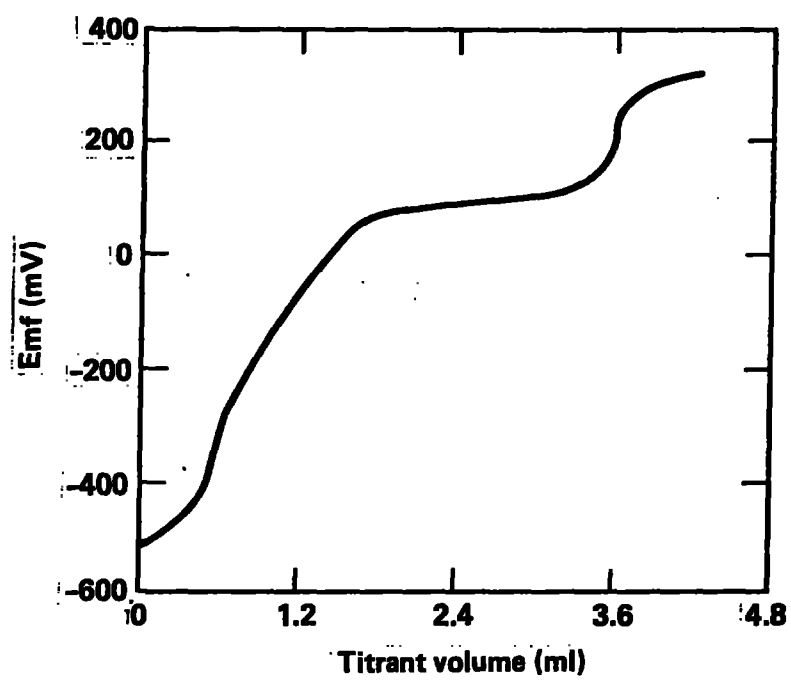
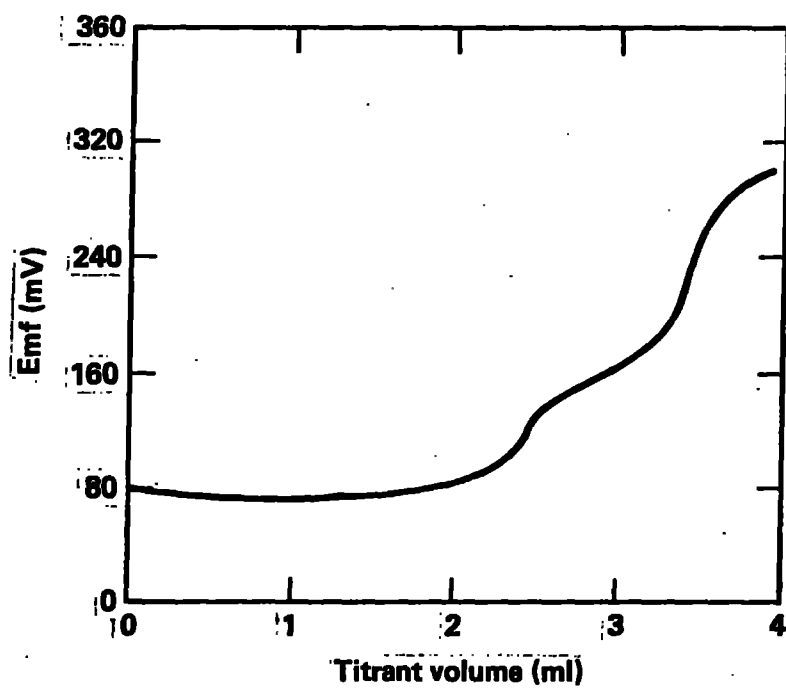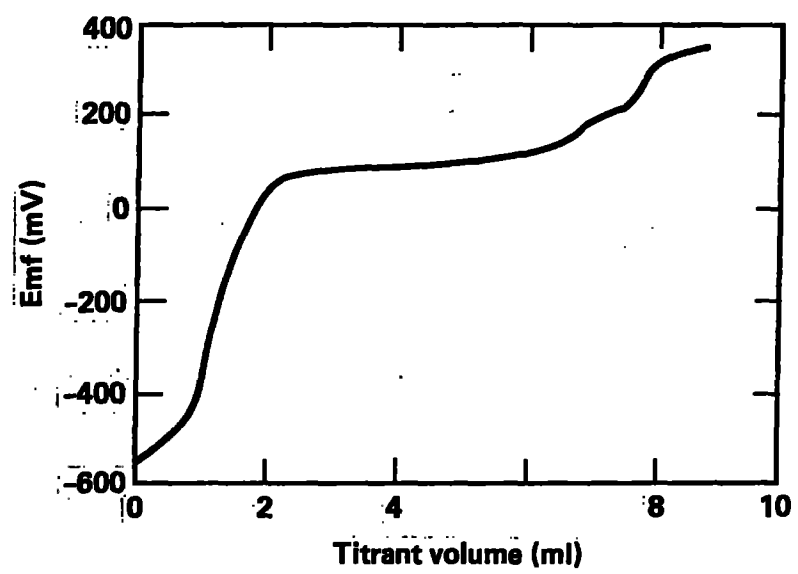Fig. 4

Table I

Comparison of Analytical Results for Gold Salt and Plating Baths

Sample	Units	Analysis by Coulometry			Analysis by Titration			means	Analysis by Gravimetry		
		Mean	n	% s	Mean	n	% s	% relative	Mean	n	% s
Gold salt 5/84	Percent.	68.07	3	0.66	68.44	3	0.25	+0.54			
Gold salt 7/84	Percent.	67.76	3	0.47	68.15	1		+0.57			
Gold salt 8/84	Percent.	67.25	3	0.36							
Gold salt 9/84	Percent.	67.40	3	0.24	68.46	3	0.12	+1.56	67.91	3	0.02
Gold strike 7/84	g/L	1.386	3	0.07	1.44	6	0.7	+3.9			
Gold strike 8/84	g/L	2.396	3	0.13	2.45	4	0.9	+2.3			
Gold strike 9/84	g/L	2.369	3	0.29	2.36	5	1.5	-0.4			
Gold strike 10/84	g/L	2.328	3	0.30	2.28	6	0.4	-1.2			
Gold Plating 7/84	g/L	15.33	3	0.85	15.73	8	0.45	+2.1			
Gold Plating 9/84	g/L	14.23	3	0.15	14.54	7	0.14	+2.1			
Pinex plating	g/L	11.20	3	0.10	11.33	6	0.51	+1.2			

Note: n is number of discrete samples of original material taken. Each mean is the result of multiple measurements on that sample.